



PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

A process for the preparation of Organosilicon Condensation Products

We, DOW CORNING CORPORATION, of Midland, Michigan, United States of America, a corporation organised under the laws of the State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the use of amine salts as catalysts for the co-condensation of silicon-bonded hydroxyl groups and silicon-bonded oxyorganic groups.

15 One object of this invention is to provide a new process for co-condensing silicon-bonded hydroxyl groups and silicon-bonded oxyorganic groups. Another object is to provide such a co-condensation system in which there is no SiOSi bond rearrangement. Another 20 object is to provide a new curing system employing an amine salt as a catalyst. Another object is to provide such a system which is operative at room temperature.

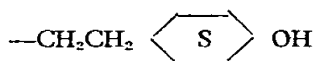
25 This invention provides a process for the production of organosilicon condensation products which comprises contacting (A) an organosilicon compound containing as functional groups both silicon-bonded hydroxyl radicals and silicon-bonded —OR¹ radicals, 30 each R¹ radical being a monovalent hydrocarbon radical or a monovalent hydrocarbon radical containing at least one function selected from ether linkages, aromatic halogen atoms, nitrile groups, hydroxyl groups and aliphatic fluorine atoms, the last being separated from 35 any silicon atom by at least three atoms, there being less than eleven total carbon atoms and ethereal oxygen atoms in each R¹, the remaining silicon valencies in said organosilicon compound being satisfied by radicals selected from 40 silicon-bonded oxygen atoms, hydrocarbon radicals and hydrocarbon radicals containing functions selected from ether linkages, aromatic halogen atoms, nitrile groups, hydroxyl groups and aliphatic fluorine atoms, the last being 45 [Price 4s. 6d.]

separated from any silicon atom by at least three atoms, (B) a compound compatible with (A) and which is (1) a salt of a phosphoric acid, the only active hydrogen atom in said acid being attached to the phosphorus through 50 an oxygen atom, and a basic amino compound, any active hydrogen in said amino compound being attached to nitrogen and any remaining nitrogen valencies being satisfied by carbon atoms, the total number of carbon atoms in 55 (1) being at least 18, or (2) a salt of a carboxylic acid, the only active hydrogen in said carboxylic acid being a part of carboxyl groups attached only to carbon atoms, and a basic 60 amino compound, any active hydrogen in said amino compound being attached to nitrogen and any remaining nitrogen valencies being satisfied by carbon atoms, the total number of carbon atoms in (2) being at least 6, whereby 65 the silicon-bonded hydroxyl radicals in (A) condense with the silicon-bonded —OR¹ radicals in (A) to form siloxane linkages and producing HOR¹ as a by-product.

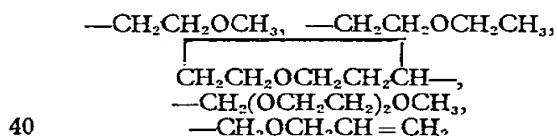
70 The organosilicon compound can be any silane, siloxane or silcarbane or any mixture thereof in which the only functional radicals attached directly to any silicon atom are both hydroxyl and —OR¹ radicals. The silicon 75 valencies not satisfied by these functional radicals can be satisfied by any atoms or radicals which do not interfere with the condensation of silicon-bonded hydroxyl groups with silicon-bonded —OR¹ groups. The silicon 80 valencies can be satisfied by oxygen atoms attached to other silicon atoms to form siloxane linkages, monovalent hydrocarbon radicals, hydrocarbon radicals which are polyvalent, i.e. 85 which have a valency higher than one, each valency of which is attached to another silicon atom to form silcarbane linkages and similar 90 monovalent and polyvalent hydrocarbon radicals containing such functions as ether linkages, aromatic halogen atoms, aliphatic fluorine atoms, hydroxyl radicals and nitrile 95 radicals. Any aliphatic fluorine atoms present

should be separated from any silicon atom by at least three carbon atoms.

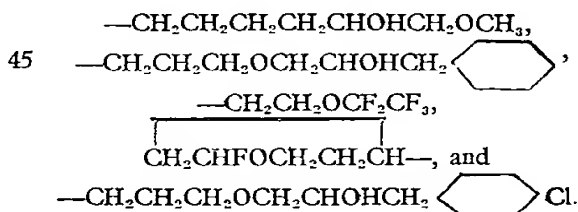
More specifically, the silicon valencies of the organosilicon compound employed in this invention can be satisfied by any monovalent radical R which can be a hydrocarbon radical, for example, any radical such as the methyl, ethyl, isopropyl, tertiary butyl, 2-ethylhexyl, dodecyl, octadecyl and myricyl radicals; any alkenyl radical such as the vinyl, allyl and hexadienyl radicals; any cycloalkyl radical such as the cyclopentyl and cyclohexyl radicals; any cycloalkenyl radical such as the cyclopentenyl and cyclohexenyl radicals; any aryl hydrocarbon radical such as the phenyl, naphthyl and xenyl radicals; any aralkyl radical such as the benzyl and phenylethyl radicals and any alkaryl radical such as the tolyl and dimethylphenyl radicals. The R radicals can also be monovalent hydrocarbon radicals containing aromatic halogen atoms such as, for example, in the 2,4,6-trichlorobenzyl, perchlorophenyl, 2 - bromonaphthyl, *p* - iodo - phenylethyl and 4 - fluorophenyl radicals; aliphatic fluorine atoms as, for example, in the 3,3,3-trifluoropropyl, α,α,α -trifluorotolyl, 3,3,4,4,5,5,5 - heptafluoropentyl and 5,5,5 - trifluoro - 2 - trifluoromethylamyl radicals; hydroxyl-containing radicals such as, for example, in the 4-ethyl-4-hydroxyhexyl, 3-hydroxyallyl, cresyl, *p*-hydroxyphenyl and



radicals; nitrile-containing radicals such as, for example, in the gamma-cyanopropyl and beta-cyanoethyl radicals and ether linkages as, for example, in the

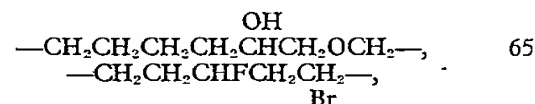
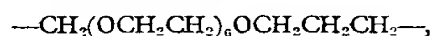


and furyl radicals. These R radicals can contain more than one of the above functions in radicals such as, for example,



These silicon valencies can also be satisfied
50 by polyvalent hydrocarbon radicals R^{11}
attached to other silicon atoms. These poly-
valent hydrocarbon radicals can contain singly

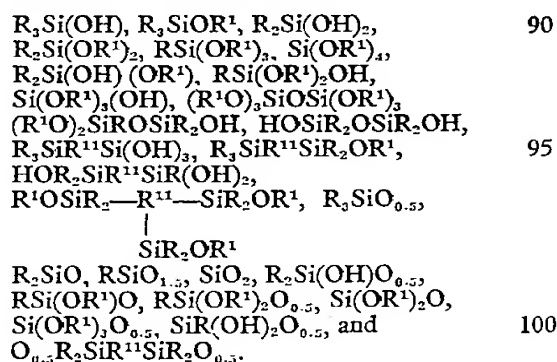
or in any combination such polyvalent radicals as methylene, vinylene, vinylidene, cyclohexylidene, phenylene, tolylene, toluenyl, toluylene, tertiary carbon atoms, and quaternary carbon atoms as well as any monovalent hydrocarbon radicals. These polyvalent hydrocarbon radicals can contain the various functions permissible in the monovalent radicals as previously described. Examples of operative polyvalent hydrocarbon radicals R^{11} containing such functions include



iodophenylene and $-\text{CH}_2-\text{C}_6\text{H}_{10}-\text{CH}_2-$.

The organosilicon polymer or monomer employed in this invention must contain both silicon-bonded hydroxyl radicals and R^1 radicals attached to silicon through silicon-oxygen-carbon linkages. The R^1 radicals can be any of the monovalent radicals set forth above for R above with the exception that in any R^1 radical the total number of carbon atoms and ethereal oxygen atoms, if any, cannot exceed ten. When the R^1 radicals are larger than this, the rate of $SiOH-SiOR^1$ condensation at room temperature is not practical.

Where R represents any of the above-described monovalent radicals and R^{11} represents any of the above-described polyvalent radicals, the organosilicon polymer or monomer employed as a starting material can contain, for example, any one or any combination of the following molecular species or can contain any one or any combination of the following types of polymer units:

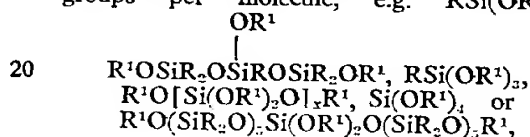


In any one molecule of the organosilicon monomer or polymer there must be at least one silicon-bonded functional radical, i.e. a hydroxyl or —OR^1 radical. While the above list does not include all the possible variations, it is sufficiently representative to show the



scope of the materials which can be employed in this invention.

The process of this invention is especially advantageous for producing liquid polysiloxanes, elastomeric gums and resins. Functionally end-blocked linear molecules, i.e. diorganopolysiloxanes, can be polymerised without bond rearrangement by the condensation of the terminal silicon-bonded functional radicals. If organosilyl end-blocking is desired, the necessary proportion of triorganosilanol or other organosilicon compound containing one silicon-bonded —OR^1 radical per molecule can be added to condense with the respective silicon-bonded —OR^1 or hydroxyl radicals on the polymer. If polyfunctionality is desired, the necessary organosilicon monomer or polymer containing more than two silicon-bonded groups per molecule, e.g. $\text{RSi(OR}^1)_3$,



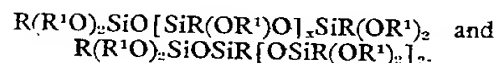
can be added to condense with the terminal silicon-bonded hydroxyl radicals on the polymer. Alternatively, the polymer can be —OR^1 end-blocked and polyfunctionality can be introduced with a polyhydroxylated organosilicon monomer or polymer, e.g. RSi(OH)_3 , $\text{HOSiR}_2\text{OSi(OH)ROSiR}_2\text{OR}$ or $\text{HO(SiR}_2\text{O)}_x\text{Si(OH)}_2\text{O(SiR}_2\text{O)}_x\text{H}$.

Siloxane elastomeric gum molecules, i.e. molecules generally having an average of about two R radicals per silicon atom, and siloxane resin molecules, i.e. molecules generally having an average of from one up to about two R radicals per silicon atom, which contain both silicon-bonded hydroxyl radicals and silicon-bonded —OR^1 radicals can be cured by the process of this invention. The increase of polymer size which takes place may be accomplished by cleaving groups leaving reactive sites which ultimately join molecules, it may be accomplished by condensation of one group or one molecule with another on an adjacent molecule, by addition reactions, etc. In this case, the polymerisation is accomplished *via* condensation. If the condensation is carried sufficiently far forward, the resin or rubber will gel or vulcanise and hence will cure.

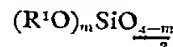
The preferred embodiment of this invention is the process employing as the organosilicon monomers and polymers a mixture of two components, one of which comprises organopolysiloxanes having at least two silicon-bonded hydroxyl radicals per molecule and the other of which comprises polyfunctional organosilicon compounds (hereinafter designated organic silicates for the sake of convenience) having at least three and preferably more silicon-bonded —OR^1 radicals per mole-

cule. The organopolysiloxane component can be a resin having an R/Si ratio of from 1 to 1.9 or a linear polymeric liquid or gum having an R/Si ratio of about 2, e.g. 1.99 to 2. If the organopolysiloxane component is a resin, the R radicals are preferably methyl and phenyl radicals such that the phenyl to silicon ratio for the organopolysiloxane component ranges from 0.25:1 to 1.5:1. Such resins inherently have good coating properties. While there can be some SiOR^1 groups present, it is preferably that they be at a minimum in order to better control the ultimate resin structure. If the organopolysiloxane component is a linear polymer liquid or gum, the R groups are preferably methyl, phenyl, vinyl, and 3,3,3-trifluoropropyl radicals. Such linear organopolysiloxanes preferably contain from about 150 to about 10,000 siloxane units for the best ultimate physical properties, but these limits are not critical to the process of this invention.

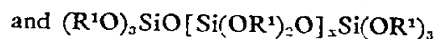
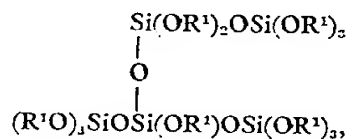
The organic silicate compounds can be composed entirely of molecules of the formula $\text{R(R}^1\text{O)}_x\text{Si}$ and solvent-soluble partial hydrolysates thereof such as



However, it is preferable that the silicate component be composed of molecules consisting essentially of units of the formula

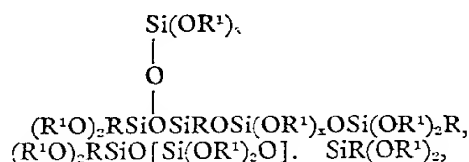
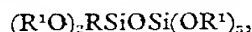


in which R^1 is as above defined and each m can be 2, 3 or 4. This formula represents both orthosilicates and polysilicates. In this specification, the term "orthosilicate" represents a compound of the formula $(\text{R}^1\text{O})_4\text{Si}$. The term "polysilicate" represents compounds having such configurations as, for example, $(\text{R}^1\text{O})_3\text{SiOSi(OR}^1)_3$, $[\text{Si(OR}^1)_2\text{O}]_x$ where y is at least 3,

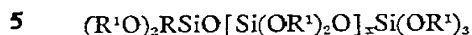


where x is at least 1. The polysilicates operative in this invention are solvent-soluble partial hydrolysates of the orthosilicates.

Mixtures of the orthosilicates, trifunctional silanes and their partial hydrolysates are operative as well as co-hydrolysates of these materials. Examples of such co-hydrolysates include



and



in which x is at least 1.

The crux of this invention resides in the discovery that certain amine salts catalyse the co-condensation of silicon-bonded hydroxyl radicals with silicon-bonded $-OR^1$ radicals. The amine salts are reaction products of basic amino compounds, i.e. ammonia or organic amines (including silylorganic amines), with phosphoric acids or carboxylic acids.

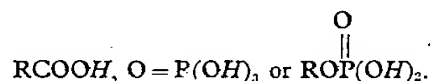
More specifically, the basic amino compound can be ammonia, a primary amine, a secondary amine or a tertiary amine. The amine can contain one or more amino groups and can also contain carbon-bonded silicon atoms and other functional organic groups which are free from active hydrogen. It is necessary that the only active hydrogen atoms, if any, be attached to nitrogen atoms. Any other active hydrogen atoms would interfere with the salt formation. The amino compound can, however, contain various non-interfering functional groups as shown in the following examples.

In short, the term "basic amino compound" means compounds containing at least one nitrogen atom attached to not more than three carbon atoms none of which are part of carbonyl, sulphonyl or nitrile groups, any remaining nitrogen valencies being satisfied by hydrogen atoms.

Specific examples of operative amines are: *o*-aminoacetanilide, iminodiacetonitrile, *m*-aminoacetophenone, allylamine, *N*-methallylamine, amylamine, *N,N*-dimethylamylamine, aniline, *p*-bromoaniline, 2,6-dinitroaniline, *m*-fluoroaniline, sym - bis - gamma - amino-propyltetramethyldisiloxane, gamma(*N*-aminoethylamino)propyldiphenylmethylsilane, *o*-iodoaniline, *o*-nitroaniline, 2,3,4,5-tetrachloroaniline, *o*-anisidine, 9-anthrylamine, 4,4'-diaminoazobenzene, anthranilonitrile, benzylamine, *p*-methoxybenzylamine, decylamine, diallylamine, dicyclohexylamine, diethylene-triamine, difurfurylamine, di-*m*-tolylamine, β -ethoxyethylamine, tetrahydrofurfurylamine, tetramethylguanidine, histamine, benzylhydrazine, *p*-bromophenylhydrazine, 1-methyl-1-phenylhydrazine, 4,4'-diaminohydrazobenzene, *p*-leucaniline, methylamine, morpholine, 5-nitronaphthylamine, 1,2-dimethyl-4-pentenylamine, *N,N*-diethyl-*p*-phenylene-diamine, piperazine, piperidine, 2-amino-pyridine, 6-nitro-*o*-toluidine, 2-amino-*p*-tolu-

nitrile, 9-phenanthrylamine, and tribenzylamine.

As stated above the salts which are operative catalysts in this invention are the reaction products of any of the basic amino compounds described above, i.e. ammonia and primary, secondary and tertiary amines, both organic and silylorganic, with either a phosphoric acid or a carboxylic acid in which any carboxyl group is attached to a carbon atom. As in the basic amino compounds where any active hydrogen atoms are attached to nitrogen atoms, so in the acids any active hydrogen atoms must be a part of the particular acid group, e.g.



An "active hydrogen" atom is one which forms methane when a compound containing acid "active hydrogen" is reacted with methyl magnesium iodide at room temperature.

The salts employed in any particular system must be compatible in that system. The degree of compatibility of any salt in any system generally depends on the total number of carbon atoms and silicon atoms and their configuration in the salt to be employed. For example, in a given system the *n*-hexylamine salt of octanoic acid is compatible while the di-*n*-hexylamine salt of succinic acid is incompatible. However, the di-eicosylamine salt of succinic acid is compatible in that system. Similarly, the mono-2-ethylhexyl amine salt of phenylphosphoric acid is compatible in a given system whereas it is necessary to go to the mono-eicosylamine salt of unsubstituted phosphoric acid to achieve compatibility in the same system. For any particular system suitable salts can be selected on the basis of compatibility.

The most compatible and therefore preferred salts are monocarboxylic acid salts which have at least six carbon atoms. Examples of the monocarboxylic acid which can be used in the preparation of these salts include the following: abietic acid, acetic acid, cyanoacetic acid, phenoxyacetic acid, acrylic acid, β -benzoylacrylic acid, angelic acid, anisic acid, *N*-acetylanthranilic acid, arachidic acid, atropic acid, *o*-bromobenzoic acid, benzoic acid, *p*-cyanobenzoic acid, 2,6-dichlorobenzoic acid, 2,5-dinitrobenzoic acid, *m*-fluoro-benzoic acid, brassidic acid, *dl*-campholic acid, capric acid, cinnamic acid, cyclohexanecarboxylic acid, cyclopropanecarboxylic acid, formic acid, 3-furanecarboxylic acid, trimethylsilylacetic acid, 5-nitro-2-furoic acid, 10-hendecenoic acid, isobutyric acid, lauric acid, levulinic acid, lignoceric acid, linoleic acid, oleic acid, stearic acid, tetrahydropyromucic acid, 3-ethyl-pentanoic acid and 2,4-xylic acid.

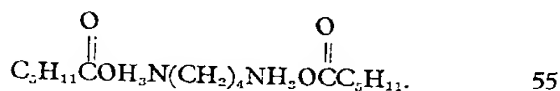
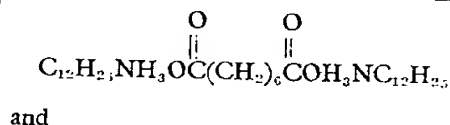
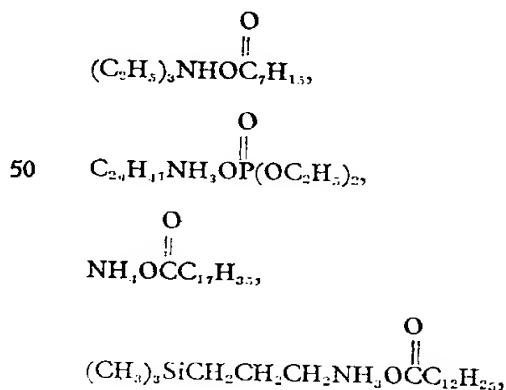
Polycarboxylic acids while not preferred can also be employed in preparing the amine salt

catalyst of this invention. Examples of such acids include: adipic acid, azelaic acid, *o*-carboxymethoxybenzoic acid, 1-camphoric acid, 1,2-cyclobutanedicarboxylic acid, sym-bis- β -carboxyethyltetramethyldisiloxane, 1,2,3,4,5,6-cyclohexanhexacarboxylic acid, 1,3-cyclopentanedicarboxylic acid, diphenic acid, ethylmalonic acid, pimelic acid, sebacic acid, succinic acid and traumatic acid. It requires more carbon atoms in an amine salt of a polycarboxylic acid to render it compatible with an organo-silicon compound operative in this invention than is the case with an amine salt of a monocarboxylic acid. For instance, in a given system *n*-hexylamine 2-ethylhexoate is very compatible and active whereas bis-eicosylamine succinate containing over three times as many carbon atoms is still less compatible and therefore less active. This problem can generally be somewhat alleviated by the use of silylorganic amine salts of these acids.

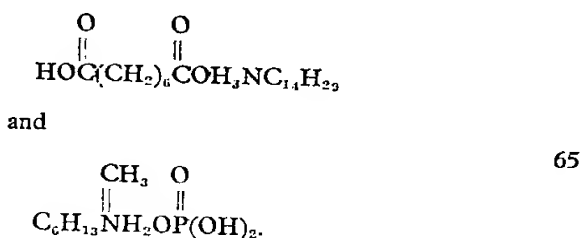
This problem of compatibility also arises with the amine salts of phosphoric acids which are also operative as catalyst in this invention. The salt can be prepared with phosphoric acid or with any acid esters of phosphorus acid such as monovalent hydrocarbon substituted phosphoric acids, e.g. phenylphosphoric, monooctadecylphosphoric or diethylphosphoric acids. An organic amine salt of phosphoric acid must contain at least 18 carbon atoms to make it sufficiently compatible in a diorganopolysiloxane to be active whereas a silylorganic amine salt may not require so much carbon to render the catalyst compatible depending on the solubility characteristics of the system.

The amine-type salts are prepared by reacting ammonia, an organic amine or an amino-organosilicon compound with a phosphoric or carboxylic acid. This can be accomplished by merely mixing the components alone in a relatively anhydrous system or by mixing the components together in a common solvent. This preparation is well known.

The amine-type salts can be normal, acidic or basic. The normal salts are those in which there are no unreacted amine or acid groups present as, for example, in



Actually, the normal salts, will often be acidic or basic depending on the relative basic and acidic characters of the amine and acid used to form the salt. This acidity or basicity can be balanced by adding an excess of the necessary amine or acid. The acidic salts are those in which there are unreacted acid groups present as, for example, in



The basic salts are those in which there are unreacted amino groups present as, for example, in



Further examples of amine salts operative as catalysts in this invention include: di-2-ethylhexylamine acetate, triphenylsilylpropylamine formate, trimethylsiloxydimethylsilhexylamine hexoate, 4,4'-diaminobenzophenone butyrate, 4,4'-diamino diphenyl ether decanoate, tri-*n*-butylamine acrylate, 3,4-dichloroaniline caproate, aniline octanoate, didodecylamine *o*-chlorophenoxyacetate, ethylamine 3-ethoxypropionate, diethylene triamine monooleate, diisopropylamine palmitate, trimethylamine stearate, benzylhydrazine hexoate, 2,5-dimethylpiperazine octoate, di(octadecylamine) sebacate, ethylene diamine di-hexoate, tetraethylene pentamine di-phosphate, 1,2-aminopropane phenylphosphate and ammonium stearate together with the salts of any other of the amines and acids shown above. These examples are by no means complete, but they do illustrate some of the types of amine-type salts which can be used. These salts can be prepared prior to their inclusion in the condensation system or they can be prepared *in situ*. For *in situ* preparation the order of addition of the acid and amine to the system is not critical.

It should be emphasised that the present

invention does not reside in the amine-type salts, which are generally well known as a class, but in the use of these salts as catalysts for the co-condensation of silicon-bonded hydroxyl groups and silicon-bonded —OR^1 radicals.

The rate of cure accomplished by this invention depends on the concentration of SiOR^1 groups and SiOH groups in the system and on the concentration of the amine salt. In other words, the number of functional radicals per molecule, the number of molecules of the organosilicon monomers and polymers present in the system and the amount of the amine salt in the system all affect the rate of the co-condensation. In order to reduce the number of variables in a given system it is preferable as stated above to employ a two-component organosilicon composition in which the organopolysiloxane component has essentially only SiOH groups and the silicate component has essentially only SiOR^1 groups. It is preferable that there be at least one molecule of the silicate component per silicon-bonded hydroxyl radical in the organopolysiloxane. It is preferable, also, that no more than 50 parts of the silicate component per 100 parts of the organopolysiloxane component be present in the system in order to better control the rate of co-condensation and the ultimate product.

As catalysts the amount of the amine salts which must be present to cause satisfactory co-condensation is not critical since even an infinitesimal amount of such salt will catalyze the reaction to a degree. However, the rate of condensation generally increases with an increase in catalyst concentration. Preferably there should be at least 0.01 per cent by weight of salt calculated on the weight of the organosilicon polymer and monomer to be condensed. An optimum rate of condensation can be achieved in any system with less than 10 per cent by weight of salt. The best range runs from 0.1 to 5.0 per cent by weight of the amine salt.

The temperature and pressure of the system are not critical but affect the rate of condensation. Generally, the rate increases as the temperature increases and as the pressure decreases.

The materials employed in this invention are either well known in the art or are easily producible by means disclosed by reference or already well known in the art. While the actual proportions of ingredients are not considered critical, it is necessary that both the organosilicon components and the amine salt be present together to produce a co-condensation or curing system. Where the three component system, i.e. organopolysiloxane, silicate and amine salt is employed, the silicate and siloxane or silicate and amine salt can be stored as combinations without appreciable change. When all three components are mixed together co-condensation starts to take place

spontaneously at room temperature. This mixture can be in organic solvent solution.

The process of this invention is useful for the polymerisation of linear polymers in the preparation of rubber-grade gums and for the curing of silicone elastomers and resins. This process is operative in the presence of organic solvents such as toluene, without rearrangement of the siloxane units.

This invention produces compounds which when employed as thin film coatings can cure to dry films on wood, metal, glass, ceramic, and the like surfaces within 24 hours at room temperature in air. Application can be by brushing, spraying or dipping. The first manifestation is surface gelation, followed by a hardening within the film. It is to be understood that a base member can be coated with the complete mixture or with some of the mixture components which are subsequently activated by introduction of the third component as by spraying a silicate, amine salt or resin solution on a pretreated base member. The compounds prepared by the process of this invention also are useful as caulking compounds.

Additives common to other organosilicon systems can also be included in the mixture employed in this invention. Generally, such additives as pigments, heat stability additives and sun-screening agents are incorporated into the organosilicon components but they can also be added separately or with the amine salt.

The following examples illustrate the invention. All viscosity measurements were made at 25°C . All quantities are measured as parts by weight. In these examples except where otherwise noted the term "EPS" designates an ethylpolysilicate having a viscosity of 12.2 cs. and containing 21.6 per cent by weight of silicon and 64.8 per cent by weight of ethoxyl radicals.

EXAMPLE 1.

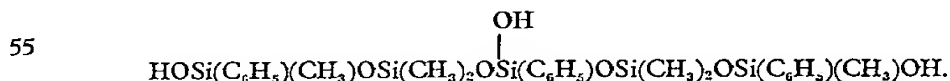
The following amine salts were prepared by mixing together the appropriate amines and acids in the proportions corresponding to the mol ratios of each component in the final salt. Where one component was solid at room temperature as in the case of myristic acid, the mixture was heated until the system was entirely liquid. There was an exothermic reaction in every case.

A PRIMARY MONOAMINE AND MONOACID

n-hexylamine 2-ethylhexoate
isobutylamine oleate
tertiary butylamine 2-ethylhexoate
tertiary butylamine decanoate
tertiary butylamine laurate
tertiary butylamine myristate
tertiary butylamine trimethyl-*n*-caproate
cyclohexylamine 2-ethylhexoate
cyclohexylamine decanoate
cyclohexylamine laurate
cyclohexylamine myristate

	tertiary octylamine 2-ethylhexoate tertiary octylamine decanoate tertiary octylamine laurate tertiary octylamine myristate	D MONO-TERTIARY AMINE + MONOACID triethylamine 2-ethylhexoate triethylamine decanoate triethylamine laurate triethylamine myristate	65
5	tertiary octylamine trimethyl- <i>n</i> -caproate tertiary nonylamine 2-ethylhexoate tertiary nonylamine decanoate tertiary nonylamine laurate tertiary nonylamine myristate	N,N-dimethyldodecylamine 2-ethylhexoate N,N-dimethyldodecylamine decanoate N,N-dimethyldodecylamine laurate N,N-dimethyldodecylamine myristate	
10	tertiary nonylamine trimethyl- <i>n</i> -caproate decylamine 2-ethylhexoate decylamine decanoate decylamine laurate decylamine myristate	triisoamylamine 2-ethylhexoate triisoamylamine decanoate triisoamylamine myristate triisoamylamine laurate tri- <i>n</i> -hexylamine 2-ethylhexoate	70
15	tridecylamine 2-ethylhexoate tridecylamine decanoate tridecylamine laurate tridecylamine myristate tridecylamine trimethyl- <i>n</i> -caproate	E DI-TERTIARY AMINE + MONOACID tetramethylethylenediamine 2-ethylhexoate (Mono Salt)	75
20	eicosylamine 2-ethylhexoate eicosylamine decanoate eicosylamine laurate eicosylamine myristate eicosylamine trimethyl- <i>n</i> -caproate	tetramethylethylenediamine decanoate (Mono Salt) tetramethylethylenediamine laurate (Mono Salt) tetramethylethylenediamine myristate (Mono Salt)	80
25	ammonium oleate ammonium stearate tertiary butylamine acetate tertiary butylamine 2,2-dimethylpropanoate <i>n</i> -hexylamine formate	F MONO-PRIMARY AMINE + POLYACID (1) monohexylamine phosphate monoeicosylamine phosphate (2) bis-hexylamine phosphate biseicosylamine phosphate	85
30	<i>n</i> -hexylamine acetate <i>n</i> -hexylamine hexoate aniline 2-ethylhexoate	(3) tris-hexylamine phosphate triseicosylamine phosphate (4) bis-eicosylamine succinate.	90
	B PRIMARY DIAMINE + MONOACID menthanediamine 2-ethylhexoate (Mono Salt) 35 menthanediamine decanoate (Mono Salt) menthanediamine laurate (Mono Salt) methanediamine myristate (Mono Salt)	When 0.02 gram-moles of each of these amine salts was mixed with 167 grams of a 60% solution in xylene of a resin co-polymer of 35 mol % of phenylmethylsiloxane units, 10 mol % of dimethylsiloxane units, 25 mol % of monomethylsiloxane units and 30 mol % of monophenylsiloxane units, the co-polymer containing 3—4% by weight of silicone-bonded hydroxyl radicals, and 5 grams of EPS, the resulting mixtures air dried to tack free gels in less than 24 hours at room temperature when applied as coatings on wood panels.	95
40	C MONO-SECONDARY AMINE + MONOACID tridecyldodecenylamine [(C ₁₃ H ₂₇)(C ₁₂ H ₂₃)NH]-2-ethylhexoate tridecyldodecenylamine decanoate tridecyldodecenylamine laurate tridecyldodecenylamine myristate tridecyldodecylamine 2-ethylhexoate		100
45	tridecyldodecylamine decanoate tridecyldodecylamine laurate tridecyldodecylamine myristate diisopropylamine 2-ethylhexoate diisopropylamine decanoate	EXAMPLE 2. 20 Parts of a polymer of the formula HO[Si(CH ₃) ₂ O] _n H having a viscosity of 2000 cs. (M.W. ≈ 21,700), 1.5 parts of EPS and 0.05 part of <i>n</i> -hexylamine 2-ethylhexoate were mixed together. The mixture gelled in about 30 minutes and cured within 24 hours to a rubbery solid at room temperature.	105
50	diisopropylamine laurate diisopropylamine myristate dibenzylamine 2-ethylhexoate dibenzylamine decanoate dibenzylamine laurate		110
55	dibenzylamine myristate di- <i>n</i> -hexylamine acetate di- <i>n</i> -hexylamine 2-ethylhexoate di- <i>n</i> -hexylamine formate di- <i>n</i> -hexylamine hexoate	EXAMPLE 3. When 20 parts of each of the following organopolysiloxanes were mixed with 1 part of EPS and 0.5 part of <i>n</i> -hexylamine 2-ethylhexoate, thin films of the resulting composi-	115
60	di- <i>n</i> -hexylamine benzoate		

- tions air-dried at room temperature within 24 hours to form hard coatings.
- 5 As a 20% by weight solution in toluene a co-polymer of 68 mol per cent of monoethylsiloxane units and 32 mol per cent. of monophenylsiloxane units and containing 0.2% by weight of silicon-bonded hydroxyl groups.
- 10 As a 50% by weight solution in toluene a co-polymer of 35 mol per cent. of phenylmethylsiloxane units, 10 mol per cent. of dimethylsiloxane units, 25 mol per cent. of monomethylsiloxane units and 30 mol per cent. of monophenylsiloxane units and containing approximately 8% by weight of silicon-bonded hydroxyl groups.
- 15 As a 50% by weight solution in xylene a co-polymer of 31.4 mol per cent. of phenylmethylsiloxane units, 34.0 mol per cent. of monomethylsiloxane units and 34.6 mol per cent. of monophenylsiloxane units and containing 0.75% by weight of silicon-bonded hydroxyl groups.
- 20 As a 75% by weight solution in toluene a mixture of (1) 50% by weight of a co-polymer of 75 mol per cent. of monomethylsiloxane units, 24 mol per cent. of dimethyl-
- siloxane units and 1 mol per cent. of trimethylsiloxane units and containing 0.4% by weight of silicon-bonded hydroxyl groups and (2) 50% by weight of a co-polymer of 25 mol per cent. of monomethylsiloxane units, 35 mol per cent. of monophenylsiloxane units, 20 mol per cent. of dimethylsiloxane units and 20 mol per cent. of diphenylsiloxane units and containing 4.8% by weight of silicon-bonded hydroxyl groups.
- 30
- 35
- 40 As a 60% by weight solution in xylene a co-polymer of 22 mol per cent. of isopropylvinylsiloxane units, 30 mol per cent. of monophenylsiloxane units, 5 mol per cent. of monohexylsiloxane units, 1 mol per cent. of monooctadecylsiloxane units, 1 mol per cent. of monocyclopentylsiloxane units, 1 mol per cent. of monobenzylsiloxane units and 40 mol per cent. of diethylsiloxane units and containing 2.0% by weight of silicon-bonded hydroxyl groups.
- 45
- 50 As a 50% by weight solution in xylene a co-polymer of 85 mol per cent. of monophenylsiloxane units, 10 mol per cent. of dimethylsiloxane units and 5 mol per cent. of diphenylsiloxane units and containing 3.5% by weight of silicon-bonded hydroxyl groups.



EXAMPLE 4.

When 1 gram of *n*-hexylamine 2-ethylhexoate was mixed with 40 grams of a 50% by weight solution in xylene of an organopolysiloxane co-polymer of 35 mol per cent. of phenylmethylsiloxane units, 10 mol per cent. of dimethylsiloxane units, 25 mol per cent. of monomethylsiloxane units and 30 mol per cent. of monophenylsiloxane units and containing 3% by weight of silicon-bonded hydroxyl groups and 4% by weight of silicon-bonded ethoxyl groups, the resulting composition air-dried at room temperature to a tack-free gel within 24 hours when applied as a coating to a cedar panel.

EXAMPLE 5.

When 20 parts of each of the following organopolysiloxanes were mixed with 1 part of EPS and 0.5 part of *n*-hexylamine 2-ethylhexoate, thin films of the resulting compositions air-dried at room temperature within 24 hours to form rubbery coatings.

80 A hydroxy-end-blocked dimethylpolysiloxane having a viscosity of 10,720 cps. (M.W. \cong 39,000).

A hydroxy-end-blocked 3,3,3-trifluoropropylmethylpolysiloxane having a viscosity of 450 cs.

85 A hydroxy-end-blocked 5,000 cs. co-polymer of 50 mol per cent. of dimethylsiloxane units, 45 mol per cent. of phenylmethylsiloxane units, 3 mol per cent. of perchlorophenylmethylsiloxane units, 1 mol per cent. of cyclohexylbenzylsiloxane units and 1 mol per cent. of dicresylsiloxane units.

EXAMPLE 6.

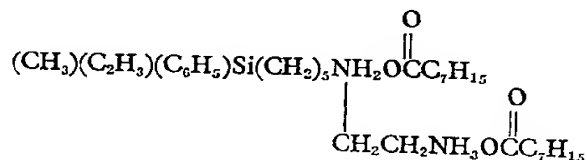
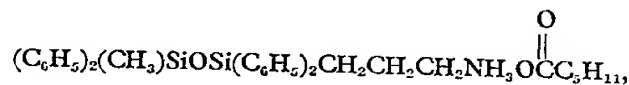
When each of the following organosilicon compounds in the amounts shown was mixed with 5 grams of *n*-hexylamine 2-ethylhexoate and 167 grams of a 60% solution in xylene of a resin co-polymer of 35 mol per cent. of phenylmethylsiloxane units, 10 mol per cent. of dimethylsiloxane units, 25 mol per cent. of monomethylsiloxane units and 30 mol per cent. of monophenylsiloxane units, said co-polymer containing 3 to 4% by weight of silicon-bonded hydroxyl radicals, the resulting compositions air-dried to a tack-free gel in less than 24 hours at room temperature when applied as coatings to wooden panels.

- | | | | |
|----|-----|----------|---|
| | 0.5 | grams of | $\text{Si}[\text{O}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5]_4$ |
| | 2 | grams of | $\text{Si}(\text{OC}_5\text{H}_{11})_4$ |
| | 1.5 | grams of | $\text{Si}(\text{OCH}_2\text{—CH}=\text{CH}_2)_4$ |
| 5 | 3 | grams of | $\text{Si}(\text{OCH}_2\text{CH}_2\text{OCH}=\text{CH}_2)_4$ |
| | 3 | grams of | $\text{Si}(\text{OC}_6\text{H}_{11})_4$ |
| | 2 | grams of | $\text{Si}(\text{OCH}_3)_3(\text{OC}_6\text{H}_4\text{Cl})$ |
| | 6 | grams of | $\text{Si}[\text{OC}_6\text{H}_3(\text{CH}_3)\text{OH}]_4$ |
| | 8 | grams of | $\text{Si}(\text{OCH}_2\text{C}_2\text{F}_5)_4$ |
| 10 | 5 | grams of | $(\text{CF}_3\text{CH}_2\text{O})_3\text{SiOSi}(\text{OCH}_2\text{CF}_3)_3$ |
| | 4 | grams of | $(\text{C}_3\text{H}_7\text{O})_3\text{SiO}[\text{Si}(\text{OC}_2\text{H}_5)_2\text{O}]_3\text{OSi}(\text{OC}_2\text{H}_5)_3$ |
| | 0.2 | gram of | $[(\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_3\text{Si}]_2\text{O}$ |
| | 4 | grams of | $\text{PhSi}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ |
| | | | CH_3 |
| | 4 | grams of | $\text{CH}_2=\text{C—CH}_2\text{Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ |
| | 6 | grams of | $\text{C}_6\text{H}_5\text{Si}(\text{OCH}_3)_3$ |
| 15 | 4 | grams of | $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2\text{OCH}=\text{CH}_2)_3$ |
| | 4 | grams of | $\text{Cl—C}_6\text{H}_4\text{—Si}(\text{OCH}_2\text{CH}=\text{CH}_2)_3$ |
| | | | |
| | 4 | grams of | $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CHSi}(\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5)_3$ |
| | 4 | grams of | $\text{CH}_3\text{CHOHCH}_2\text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ |
| | 4 | grams of | $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{O}[\text{Si}(\text{OC}_4\text{H}_9)_2\text{O}]_3[\text{Si}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)\text{O}]_2\text{Si}(\text{OC}_3\text{H}_7)_3$ |
| 20 | 4 | grams of | $[\text{Si}(\text{OC}_2\text{H}_5)_2\text{O}]_4$ |

EXAMPLE 7

When 0.02 gram-moles of the following amine salts were substituted for the amine salts

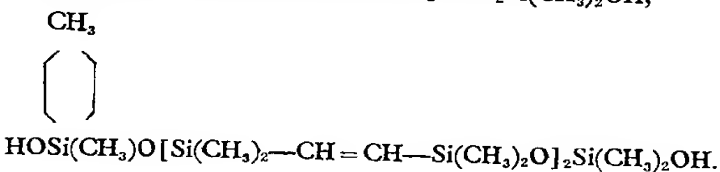
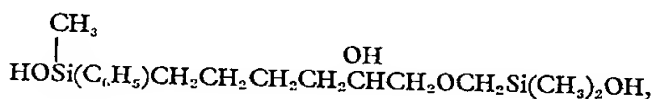
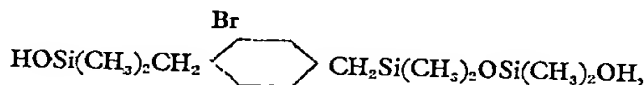
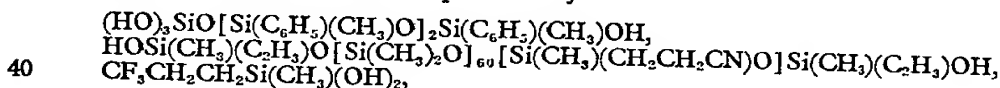
employed in Example 1, similar tack-free coatings resulted.



EXAMPLE 8.

30 When the following hydroxyl-end-blocked organosilicon compounds were each mixed with approximately 2 per cent. by weight of *n*-hexylamine 2-ethylhexoate and 8 per cent. by

weight of EPS calculated on the weight of the organosilicon compound, each of the resulting compositions cured to a tack-free gel within 24 hours at room temperature.

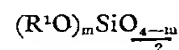


WHAT WE CLAIM IS:—

1. A process for the production of organo-silicon condensation products which comprises contacting (A) an organosilicon monomer, polymer or mixture thereof containing both silicon-bonded hydroxyl radicals and silicon-bonded —OR^1 radicals, each R^1 radical being a monovalent hydrocarbon radical or a monovalent hydrocarbon radical containing at least one function selected from ether linkages, aromatic halogen atoms, nitrile groups, hydroxyl groups and aliphatic fluorine atoms, the last being separated from any silicon atom by at least three atoms, there being less than eleven total carbon atoms and ethereal oxygen atoms in each R^1 , the remaining silicon valencies being satisfied by radicals selected from silicon-bonded oxygen atoms, hydrocarbon radicals and hydrocarbon radicals containing functions selected from ether linkages, aromatic halogen atoms, nitrile groups, hydroxyl groups and aliphatic fluorine atoms, the last being separated from any silicon atom by at least three atoms with (B) a compound compatible with (A) and which is (1) a salt of a phosphoric acid, the only active hydrogen atoms in said acid being attached to the phosphorus through an oxygen atom, and a basic amino compound, any active hydrogen in said amino compound being attached to nitrogen and any remaining nitrogen valencies being satisfied by carbon atoms, the total number of carbon atoms in (1) being at least 18, or (2) a salt of a carboxylic acid, the only active hydrogen in said carboxylic acid being a part of carboxyl groups attached only to carbon atoms, and a basic amino compound, any active hydrogen in said amino compound being attached to nitrogen and any remaining nitrogen valencies being satisfied by carbon atoms, the total number of carbon atoms in (2) being at least 6, whereby the silicon-bonded hydroxyl radicals (A) condense with the silicon-bonded —OR^1 radicals in (A) to form siloxane linkages and producing HOR^1 as a by-product.

2. A process for the production of organo-silicon condensation products which comprises mixing together (1) an organopolysiloxane containing an average of at least one silicon-bonded hydroxyl radical per molecule and from 1.0 to 3.0 monovalent hydrocarbon radicals

per silicon atom, (2) at least 0.01 part per 100 parts of (1) of an organo-silicon monomer, polymer or mixtures thereof, of the general formula



in which R^1 is a monovalent hydrocarbon or hydrocarbon ether radical containing less than eleven carbon or total carbon and oxygen atoms and m is 2, 3 or 4, and (3) at least 0.01 part per 100 parts of (1) of a salt of a carboxylic acid, the only active hydrogen in said carboxylic acid being a part of carboxyl radicals attached only to carbon atoms, and a basic amino compound, any active hydrogen in said amino compound being attached to nitrogen and any remaining nitrogen valencies being satisfied by carbon atoms, the total number of carbon atoms in (3) being at least 6, whereby the silicon-bonded hydroxyl radicals in (1) condense with the silicon-bonded —OR^1 radicals in (2) to form siloxane linkages and producing HOR^1 as a by product.

3. A process as claimed in claim 2 or 3, wherein (1) is an organopolysiloxane having an average of at least two silicon-bonded hydroxyl radicals per molecule and from 1.0 to 1.9 methyl and phenyl radicals per silicon atom of which from 0.25 to 1.5 radicals per silicon atom are the phenyl radicals.

4. A process as claimed in any one of the preceding claims wherein the mixture is allowed to condense or to cure.

5. A process as claimed in any one of the preceding claims 1, 2 and 4 wherein the organopolysiloxane (1) is essentially a diorganopolysiloxane.

6. A process for the production of organo-silicon condensation products substantially as described with reference to any one of the Examples.

7. Organosilicon condensation products when produced by the process claimed in any one of the preceding claims.

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